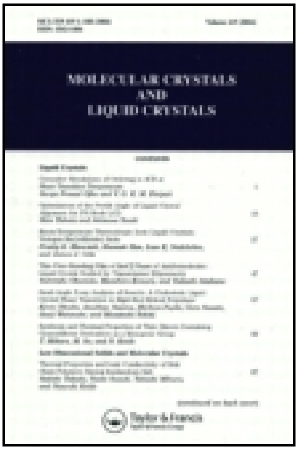

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Self-Organized Ion-Conductive Liquid Crystals: Lithium Salt Complexes of Mesogenic Dimer Molecules Exhibiting Smectic A Phases

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Liquid-crystalline dimeric molecules consisting of rigid mesogenic cores and flexible oxyethylene spacers have been prepared. The ethoxy carbonyl and alkoxy groups are attached to the ends of the mesogenic cores. These molecules have been complexed with lithium triflate, resulting in thermal stabilization of the mesophases. Ionic conductivities along the direction perpendicular to the molecular director of the smectic A phases have been measured for these complexes.

Keywords: Liquid Crystal; Smectic A; Ionic Conductivity; Poly(ethylene oxide); Lithium Ion; Self-Organization

INTRODUCTION

Liquid crystals are self-organized anisotropic functional materials.[1] The use of anisotropy of liquid crystals for charge or mass transport has great potential for future application of self-organized materials.[2-4] On the other hand, high ionic conductivities of complexes of amorphous poly(ethylene oxide)s (PEOs) and alkali metal salts have attracted much attention for the fabrication of new electrochemical materials.[5,6] Recently, PEOs have been modified by mesogenic moieties to develop new functional ion-transporting materials.[7-10] We designed and prepared mesomorphic complexes consisting of lithium triflate ($LiOSO_2CF_3$) and dimeric molecules containing oxyethylene moieties to fabricate anisotropic ion-conductive materials forming self-organized layered structures.[9,10] The mesomorphic behavior and ionic conductivities were examined for these complexes. We succeeded in measuring ionic conductivities along the direction perpendicular to the molecular director of the homeotropically aligned smectic phases which were thermally stabilized through ion-dipole interactions (Figure 1). In this case, nanometer level phase segregation between oxyethylene and mesogenic moieties is a key for anisotropic ion conduction. In the present study, complexes of dimer molecule **1** having the ethoxy carbonyl groups with lithium triflate ($LiOSO_2CF_3$) have been prepared (Figure 2). The thermal properties and the ionic conductivities of the lithium salt complexes of **1** have been compared with those of **2** having the octyloxy terminal groups, which were reported previously.[10]

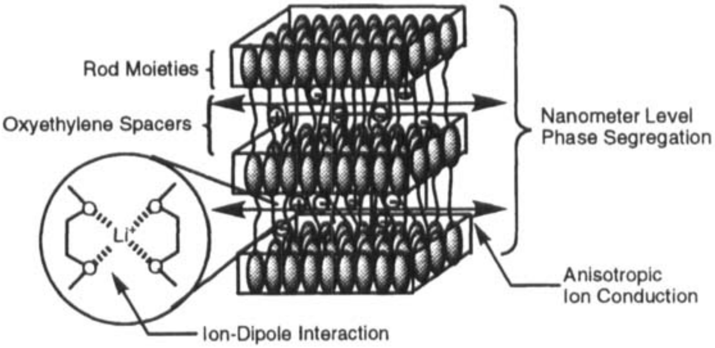

FIGURE 1 Schematic illustration of anisotropic ion conduction in self-organized smectic layer structures.

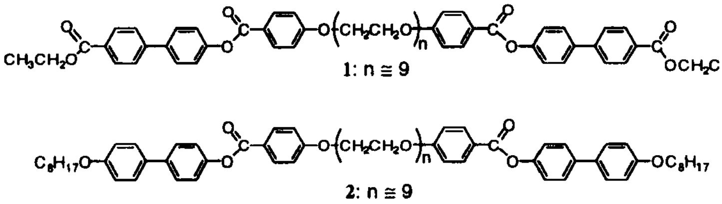

FIGURE 2 Molecular structures of liquid-crystalline dimers.

RESULTS AND DISCUSSION

We previously reported self-organization behavior of the complexes of **2** containing the octyloxy groups with $LiOSO_2CF_3$.[10] It was expected that the induction of wider temperature ranges of smectic A (S_A) phases led to higher ionic conductivities in wider ranges. For monomeric esters **3**[11] and **4**[12] containing the same mesogen, the effect of the ethoxy carbonyl group on the mesomorphic behavior is compared with that of the octyloxy group in Figure 3. Mesogenic compound **3** exhibits an S_A phase while compound **4** only shows a nematic (N) phase. Thus compound **1** is designed for dimer complexes exhibiting wider temperature ranges of the smectic A phases. The transition temperatures of **1**, **2** and their lithium salt complexes are given in Table 1. The single component of **1** having the ethoxy carbonyl terminal groups exhibits smectic C (S_C), S_A, N, and ordered smectic phases. In contrast, an S_A phase is not seen for **2** having the octyloxy terminal groups. Compound **2** shows S_C, N,

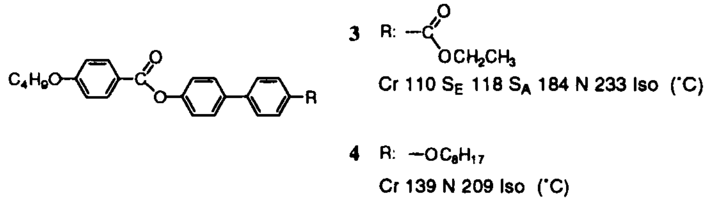

FIGURE 3 Molecular structures of mesogenic monomeric compounds.

and ordered smectic phases. Complexation of these compounds with lithium triflate results in the increase of the isotropization temperatures (T_i) and the induction of wider temperature ranges of the S_A phases. Lithium salt complexes of **1** exhibit the lower temperatures of transitions to the S_A phases than those of **2**. The increase of the glass transition temperatures with the increase of the lithium salt concentration is observed for both complexes **1** and **2**. This behavior can be attributed to the interaction between the oxyethylene moieties and the lithium cations.[10,13]

TABLE 1 Transition Temperatures of Lithium Salt Complexes of Mesogenic Dimeric Compounds **1** and **2**.

	$[Li^+]/[CH_2CH_2O]$	phase transition behavior[a]					
1	0		S_X 94	S_C 98	S_A 140	N 148	I
1/$LiOSO_2CF_3$	0.05			G -25	S_X 91	S_A 160	I
1/$LiOSO_2CF_3$	0.20			G 14	S_X 91	S_A 180	I
2[b]	0	G -45	S_X 82	S_X 90	S_C 121	N 135	I
2/$LiOSO_2CF_3$[b]	0.05	G -26	S_X 77	S_X 85	S_C 129	S_A 144	I
2/$LiOSO_2CF_3$[b]	0.20	G 8	S_X 65	S_X 72	S_X 103	S_A 175	I

[a]Transition temperatures (°C) on the second heating. G: glassy; S: smectic; N: nematic; I: isotropic. S_X: unidentified ordered smectic phase. [b]Ref. [10].

Figure 4 plots the transition temperatures of the lithium salt complexes of **1** as a function of the ratio of the lithium salt to the oxyethylene unit ($[Li^+]/[CH_2CH_2O]$). No phase separation is observed for the mixtures of dimeric molecule **1** and lithium triflate. The S_A phases have been stabilized by the complexation with lithium triflate. The maximum T_i is seen at 180 °C for the complex with the salt ratio of 0.20 ($[Li^+]/[CH_2CH_2O] = 0.20$). The maximum degree of the positive deviation is 32 °C. In contrast, the complexes of **2** give the highest T_i for the salt ratio of 0.40.[10] Further addition of lithium triflate results in the decrease of T_i. The S_X-S_A transition temperatures decrease with the increase of the salt concentration.

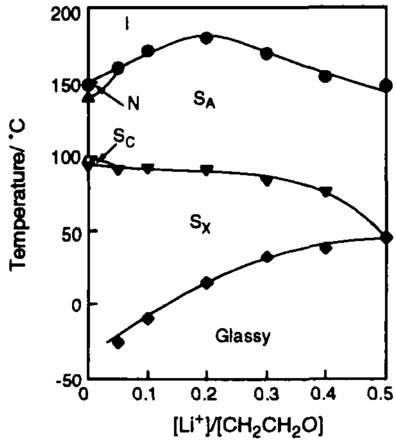

FIGURE 4 Dependence of the phase transition temperatures of lithium salt complexes of **1** as a function of the ratio of lithium triflate to the oxyethylene unit ($[Li^+]/[CH_2CH_2O]$) on the second heating scan.

Ion conductive properties have been examined for the lithium salt complexes of dimeric mesogenic molecules **1** and **2**. A glass plate with comb-shaped gold electrodes and a pair of indium tin oxide (ITO) electrodes have been employed for the measurements. A homeotropically aligned monodomain of the S_A phase has been formed on the glass surface with gold electrodes. In this case, ionic conductivities along the direction perpendicular to the molecular director of the S_A phases have been measured for the aligned samples. In contrast, for the ITO electrodes, polydomain formation is observed. Figure 5 presents the ionic conductivities of the lithium salt complexes of **1** and **2** ($[Li^+]/[CH_2CH_2O] = 0.05$). For the monodomain samples of the lithium salt complexes in the S_A phases, the ionic conductivities of the complexes of **1** having the ethoxy carbonyl terminal groups are higher than those of the complexes of **2** having the octyloxy terminal groups. The highest ionic conductivity observed for the lithium salt complex of **1** is 1.6×10^{-4} S cm^{-1} at

142 °C. For the polydomain sample of the lithium salt complex of **1** on the ITO electrodes, ionic conductivities drastically decrease with the decrease of temperatures. Formation of stable long range conductive pathways in homeotropically aligned S_A phases should contribute to high ionic conductivities.

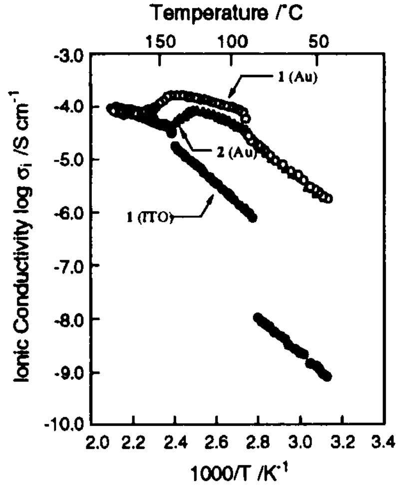

FIGURE 5 Ionic conductivities of the complexes of **1** and **2** with $LiOSO_2CF_3$.

The incorporation of the ethoxy carbonyl groups at the terminal position of the dimeric molecules leads to the induction of higher T_is and wider temperature ranges of the S_A phases for the lithium salt complexes. Ionic conductivities of lithium salt complexes are increased by the replacement of the alkoxy groups with the ethoxy carbonyl groups. These materials are useful for anisotropic ion conduction in self-organized smectic layer structures.

EXPERIMENTAL

Differential scanning calorimetry (DSC) measurements were carried out on a Mettler DSC 30. Heating and cooling rates were 10 °C min^{-1}. Lithium salt complexes were prepared by slow evaporation of the THF solution of dimeric compounds and requisite amounts of lithium triflate. The details on the measurements of ionic conductivities and the preparation of dimer molecules **1** and **2** were described in our previous papers.[9,10]

α,ω-Bis{4-[(4'-ethoxycarbonyl-1,1'-biphenyl-4-yl)oxy-carbonyl]phenyl}oligo(oxyethylene) (1). A flask equipped with a magnetic stirring bar, an argon inlet, and a reflux condenser, was charged with α,ω-bis(4-carboxyphenyl)oligo(oxyethylene) (2.3 g, 3.5 mmol). Then $SOCl_2$ (10 mL) was added at room temperature. The resulting solution was stirred and heated to reflux for 4 h under gentle purging with argon *via* the inlet. Then the excess of $SOCl_2$ was fully removed by distillation *in vacuo*. The residue was dissolved in dry THF (5.0 mL), and the flask was cooled at 0 °C using an ice-water bath. To this solution was added dropwise a solution of ethyl 4'-hydroxy-1,1'-biphenyl-4-yl carboxylate (1.7 g, 7.0 mmol) and triethylamine (3.0 mL) in dry THF (10 mL) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 12 h. The solvent was evaporated and the residue was thoroughly washed with $CHCl_3$. The combined organic solution was washed with a 5% aq. HCl solution and a sat. aq. NaCl solution, successively, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (eluent: $CHCl_3$ followed by $CHCl_3$/methanol = 20/1) afforded **1** (2.6 g, 2.4 mmol) in a yield of 69% as a white colorless solid. ^1H NMR ($CDCl_3$, 270 MHz): δ = 1.42 (t, J = 7 Hz, 6 H), 3.64-3.77 (m, 28 H), 3.90 (t, J = 5 Hz, 4 H), 4.23 (t, J = 5 Hz, 4 H), 4.41 (q, J = 7 Hz, 4 H), 7.01 (d, J = 9 Hz, 4 H), 7.31 (d, J = 9 Hz, 4 H), 7.66 (d, J = 9 Hz, 4 H), 7.67 (d, J = 9 Hz, 4 H), 8.12 (d, J = 9 Hz, 4 H), 8.16 (d, J = 9 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.3, 60.9, 67.6, 69.4, 70.5, 70.8, 114.3, 121.6, 122.2, 126.9, 128.3, 129.2, 130.0, 132.2, 137.5, 144.6, 151.0, 163.1, 164.7, 166.4. IR (KBr): 772, 1007, 1104, 1175, 1209, 1285, 1607, 1707, 1727, 2341, 2360, 2870 cm^{-1}.

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